

UDC 666.1.036.6

MECHANISM OF FOAM-GLASS FORMATION

V. E. Manevich¹ and K. Yu. Subbotin¹Translated from *Steklo i Keramika*, No. 5, pp. 18–20, May, 2008.

The mechanism of thermal dissociation of a carbon foaming agent is determined and the parameters of the foam-glass formation process are calculated. Promising directions for improving the foaming process are determined.

Foam glass is one of the most promising heat and sound insulating materials [1]. This material is distinguished by a complex of properties such as low thermal conductivity, high strength, wide temperature range for applications, heat resistance, and longevity. The fabrication and use of foam glass are ecologically clean.

the technological regime for producing foam glass is characterized by three basic stages: heating a mixture of glass powder and foaming agent up to the foaming temperature — stage I; foaming — stage II; and, fixation of the macrostructure (point A) and firing of a block — stage III (see Fig. 1a).

Concerning the heat and mass transfer processes, intense heating of the mixture occurs at stage I, when the volume of the mixture changes negligibly and the air temperature and pressure in the mixture increase. At the end of this stage the surface of the mixture dispensed into a mold or onto a platform fuses. At stage II the intensity of the heat-transfer processes decreases and the oxidation reactions of foaming are activated. The shapes of the parts (foam glass) are fixed as the surface of the glass fuses. At stage III slow heat transfer from the foam glass into the surrounding medium occurs and the glass is held at a definite temperature in order for the stresses to relax — annealing.

We shall examine the thermodynamics of the processes occurring at the three stages in the production of foam glass (see Fig. 1b).

We make the following assumptions [2]:

the processes are thermodynamically reversible;

the gases released during foaming satisfy the Mendeleev – Clapeyron law, i.e., they are ideal gases:

$$PV = nRT,$$

where P is the pressure, Pa; V is the volume of the gas, m³; n is the amount of matter, moles; R is the universal gas con-

stant, $R = 8.314 \text{ J}/(\text{mole} \cdot \text{K})$; T is the temperature, K; the heating and tempering processes are isochoric, i.e., they occur without a change in the volume of the gas; and, the foaming process is isothermal, i.e., it occurs without a change of temperature.

These assumptions are all completely justified for the macroprocesses occurring during the deformation of foam glass under real conditions.

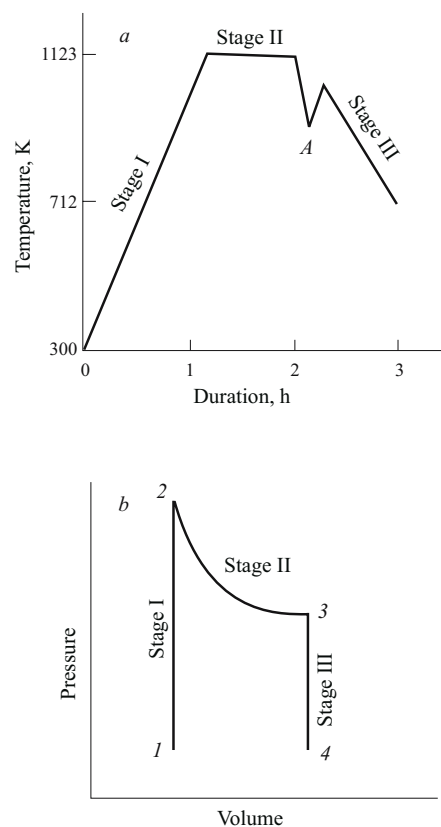


Fig. 1. Temperature – time (a) and thermodynamic (b) characteristics of the foaming process.

¹ Stromizmeritel' JSC, Moscow – Nizhny Novgorod, Russia.

We shall evaluate the completeness of the combustion of carbon and the composition, volume, and pressure of the gases released. For this, we separate a 100 g element of mass, filled with a mix with the composition $G_{gl} = 98.3$ g of glass powder and $G_c = 1.7$ g of carbon, in the space of the mold (ribbon).

The following reactions are thermodynamically most likely to occur when carbon is used as the foaming agent:



The kinetic characteristics of the reactions are [3, 4]: activation energy $E_1 = 1.24$ kJ/mole, $E_2 = 128$ kJ/mole, equilibrium reaction rate constants $k_{01} = 0.018 \times 10^6 \text{ sec}^{-1}$ and $k_{02} = 0.1 \times 10^7 \text{ sec}^{-1}$.

The volume of gas generated during foaming of the glass is given by

$$V = V_0 \sum_i c_{0i} [1 - \exp(-k_i t)],$$

where V_0 is the amount of gas which can be released when the decomposition of carbon is completed, $V_0 = 50\%$ for gaseous carbons, $V_0 = 31\%$ for brown coal, c_{0i} is a coefficient, $\sum c_{0i} = 1$, $c_{01} = 0.15$ for the reaction (1), $c_{02} = 0.85$ for the reaction (2), t is the duration of stage II (foaming), $t = 1$ h,

$$k_i = k_{i0} \exp\left(-\frac{E}{RT_{fm}}\right), \quad (3)$$

where k_i is the rate constant of the i th reaction, T_{fm} is the foaming temperature (stage II).

A calculation using the relation (3) gives $V_{b.c} = 25\%$ for brown coal $V_{g.c} 41.5\%$ for gaseous carbons.

It follows from the data obtained that different grades of carbon differ substantially with respect to the volume of gas released during thermal dissociation. The same conclusion can also be drawn with respect to solid carbonates and liquid hydrocarbons.

The initial batch of foam glass contains glass powders, powder or slip of the foaming agent, and air trapped by them. During heat treatment the foaming agent undergoes thermal dissociation with formation of combustion products — the reactions (1) and (2). Small bubbles form and grow rapidly in the volume as result of heating and diffusion of gases from the volume of the charge, partially escaping into the furnace medium and partially remaining in the foam-glass mass. At foaming temperature 850°C the fused charge remains very viscous and large volumes of gases from the products of thermal dissociation of the foaming agent can pass from the volume of the charge into the furnace space only under very high pressure.

Let us examine the balance of mass during the foaming process.

The mass of carbon dioxide in the reaction (1):

$$G_{CO_2} = 1.7 \times 0.415 \times 0.15 = 0.106 \text{ g.}$$

The mass of carbon monoxide in the reaction (2):

$$G_{CO} = 1.7 \times 0.415 \times 0.85 = 0.600 \text{ g.}$$

The mass of oxygen:

$$G_{O_2} = \frac{1.7 \times 32}{12} \times 0.415 = 0.188 \text{ g.}$$

The mass of nitrogen:

$$G_{N_2} = 0.282 \frac{79}{21} = 7.07 \text{ g.}$$

The masses of O_2 , C , N_2 , CO , and CO_2 are, respectively, $M_{O_2} = 32$, $M_C = 12$, $M_{N_2} = 28$, $M_{CO} = 28$, and $M_{CO_2} = 44$.

The ratio of the nitrogen and oxygen contents in air is 79 : 21.

The coefficients of additivity of the mass of the products of combustion of carbon:

$$m_{CO} = \frac{G_{CO}}{G_{CO} + G_{CO_2} + G_{N_2}} = 0.077;$$

$$m_{CO_2} = 0.014; \quad m_{N_2} = 0.909.$$

The specific gas constant for the products of combustion:

$$R_g = R_{un} \left(\frac{m_{CO}}{M_{CO}} + \frac{m_{CO_2}}{M_{CO_2}} + \frac{m_{N_2}}{M_{N_2}} \right) = 279.84 \text{ J/(kg} \cdot \text{K)}.$$

The volume of the sample charge:

$$V_{ch} = \frac{G_{ch}}{d_{ch}} = 71.4 \text{ cm}^3,$$

where d_{ch} is the density of the charge, $d_{ch} = 1.4 \text{ g/cm}^3$.

The volume of the glass powder $98.3/2.5 = 39.3 \text{ cm}^3$.

The carbon volume:

$$V_c = 1.7/1.5 = 1.1 \text{ cm}^3.$$

The air volume:

$$V_{air} = 71.4 - 39.3 - 1.1 = 31 \text{ cm}^3.$$

The mass of the foam glass, using gaseous carbons as the foaming agent, whose combustion, as shown above, amounts to 41.5%:

$$G_{fg} = G_{gl} + G_c - G_{cc} = 99.17 \text{ g,}$$

where G_{fg} , G_g , G_c , and G_{cc} are the mass of the foam glass, glass, carbon, and combusted carbon, respectively.

The volume of the foam glass:

$$V_{fg} = \frac{G_{fg}}{d_{fg}} = 620.56 \text{ cm}^3,$$

where d_{fg} is the density of the foam glass, $d_{fg} = 0.16 \text{ g/cm}^3$.

The volume of the glass phase in the foam glass:

$$V_g = V_{fg} - V_{gl} - (V_c - V_{cc}) = 521.27 \text{ cm}^3.$$

Starting from the ideal-gas equation:

$$G_g = \frac{PV_g}{R_g T} = 0.621 \text{ g},$$

we find the mass G_g of the gasses in the sample of foam glass ($P = 1 \text{ atm}$ (104 kgf/cm^2), temperature $T = 300 \text{ K}$).

During stage II of the foaming process (see Fig. 1) the temperature of the sample remains constant:

$$\frac{P_2 V_2}{T_2} = G_3 R_3, \quad (4)$$

where $V_2 = V_1$, i.e., the volume of the combustion products equals the volume of the air which they displace; T_2 is the foaming temperature; $T_2 = 1123 \text{ K}$; $G_3 = G_g$; $R_3 = R_g$.

We shall evaluate the pressure of the gases in the foam glass at the onset foaming (the point 2 in Fig. 1b) according to the relation (4):

$$P_2 = \frac{G_g R_g T}{V_2} = 62.95 \text{ atm}.$$

Since the annealing process (stage III) is isochoric, i.e., $V = \text{const}$, $P_3 T_3 = P_4 T_4$, at the end of annealing the temperature $T_4 = 300^\circ\text{C}$ and the pressure $P_4 = 1 \text{ atm}$.

Hence, at the start of annealing $P_3 = 3.74 \text{ atm}$, i.e., the pressure decreases relative to the foaming pressure by almost a factor of 20.

The radius of the gas bubbles can be calculated from the relation

$$P_{fg} = P_g - \frac{2\sigma}{r} - \frac{4Mv_{gl}}{r},$$

where P_{fg} is the pressure in the foam glass; P_g is the pressure in the gas phase, formed during thermal decomposition of carbon; σ is the surface tension, $\sigma = 40 \times 10^{-2} \text{ N/m}$; v_{gl} is the velocity of the glass, $v_{gl} = 0$; r is the radius of a bubble.

Then, for $P_{fg} = 1 \text{ atm}$, $P_g = 62.95 \text{ atm}$, the radius of a bubble appearing at the end of stage I is approximately $2.2 \times 10^{-2} \text{ mm}$. Next, the bubble grows and the total amount of the released gas at the end of stage II is determined from the following considerations:

$$P_3 V_3 = P_2 V_2; \quad V_3 = 5232 \text{ cm}^3,$$

i.e., a portion of these gases escapes into the atmosphere in the foaming furnace.

We shall now examine the balance of heat during the foaming process [5].

The heat of the reactions (1) and (2), calculated per 1 kg of combusted carbon, equals 28604.2 and 4923.7 kJ/kg (6832 and 1176 kcal/kg). The total amount of heat released is 33527.9 kJ/kg (8008 kcal/kg).

An amount of heat equal to 23.9 kJ (5.7 kcal) is released per $1.7 \times 0.415 = 0.71 \text{ g}$ of combusted carbon.

The enthalpy of the combustion products:

$$G_g c_g = G_{N_2} c_{N_2} + G_{CO_2} c_{CO_2} + G_{CO} c_{CO} = 1.93 \text{ kJ/K} (0.46 \text{ kcal/K}),$$

where c is the specific heat.

The amount of heat all components at stage I:

$$Q = [G_{gl} c_{gl} + (G_c - G_{cc}) c_c + G_g c_g] (T_1 - T_3) = 87.9 \text{ kJ} (21 \text{ kcal}).$$

Thus, the combustion of carbon contributes only $(5.7 + 0.46)/21 = 0.27$ of the heat (29%) required for foaming. This suggests that one must look for foaming agents that give a larger heat effect, for example, thermite mixtures.

Some practical conclusions can be drawn from this analysis of the mechanism of foaming of glass.

Carbons are not sufficiently effective foaming agents. An amount equal to 20 – 40% of the initial carbon is combusted with gases being released. Liquid hydrocarbons could be more intense foaming agents. Considering the high rate and completeness of their combustion, they should be used together with modifiers which have a retarding effect on the combustion reaction rate.

When carbons undergo thermal decomposition they make a negligible contribution to the consumption of heat for foaming. However, a substantial pressure develops in the gas phase, which makes it possible to overcome the surface tension of the glass, which is viscous at its foaming temperature.

Interesting results can be expected from the use of thermite mixtures as foaming agents. Such mixtures combust to a high degree of completeness, they give rise to intense formation of bubbles and high pressure in the bubbles, and they contribute a substantial heat effect of the reactions.

REFERENCES

1. V. E. Manevich and K. Yu. Subbotin, "Foam glass and the problems of energy conservation," *Steklo Keram.*, No. 4, 3 – 6 (2008).
2. V. I. Babushkin, G. M. Matveev, and O. P. Mchedlov-Petrosyan, *Thermodynamics of Silicates* [in Russian], Stroiizdat, Moscow (1965).
3. A. A. Agroskin and V. B. Gleibman, *Thermal Physics of Solid Fuel* [in Russian], Nedra, Moscow (1980).
4. Yu. Fal'be, *Chemicals from Carbon* [Russian translation], Khimiya, Moscow (1980).
5. L. S. Éigenson, T. I. Beloborodova, B. I. Borisov, and E. G. Frolova, *Thermal Principles of Glass Formation* [in Russian], Stroiizdat, Moscow (1959).